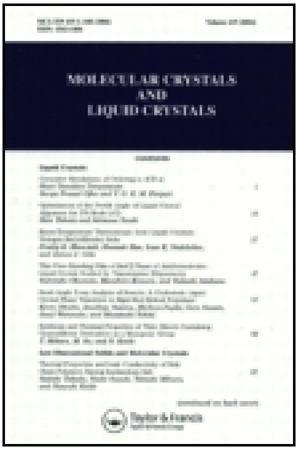

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Crystal Structure of a Non-Conductive Non-Stoichiometric Tetrathiafulvalenium Salt: $(TTF)_3(BF_4)_2$

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Crystal Structure of a Non-Conductive Non-Stoichiometric Tetrathiafulvalenium Salt: $(TTF)_3(BF_4)_2$

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$(TTF)_3(BF_4)_2$ crystallizes in the triclinic system, space group $P\bar{1}$, $a = 8.017(3)$, $b = 8.601(1)$, $c = 11.635(2)$ Å, $\alpha = 108.79(1)$, $\beta = 100.96(2)$, $\gamma = 99.09(2)°$, $Z = 1$. The TTF entities are stacked in parallel columns arranged into parallel layers alternating with layers of BF_4^- anions. A TTF stack is constituted of $(TTF^+)_2$ diads interspersed with TTF° monads; the TTF^+–TTF^+ overlap is of the ring-over-ring type while the TTF^+–TTF° overlap is of the bond-over-ring type. These features explain the low conductivity ($\sigma_{powder} = 2 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$) of this apparently non-stoichiometric TTF salt.

INTRODUCTION

Organic conductors derived from TTF-like molecules (TTF = 1,4,5,8-tetrathiafulvalene) have been recently, extensively and successfully studied:[1] for example, the observation of superconductivity in $(TMTSF)_2ClO_4$[2] is a most important result in this field. Although the requirements to achieve metallic behaviour form the subject of conceptual controversies,[3] simple guidelines may be used for evaluating prospective candidate systems: (i) close stacking with uniform separation in one-dimensional segregated chains of the donors and acceptors or counterions (that does not preclude interchain interactions), (ii) mixed valence state obtained through partial charge transfer between donors and acceptors or counterions. Most of the highly conductive $(TTF)X_x$ organic salts[4-8] have these features. Wudl[5] has described the synthesis and electrical properties of $(TTF)_3(BF_4)_2$, or $(TTF)(BF_4)_{0.67}$; although this salt seems at first glance to possibly meet the above criteria, it shows a surprisingly low conductivity ($\sigma_{powder/300K} = 2 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ [9]). We report here the full X-ray structure determination of this compound which gives the clue to its electrical behaviour.

EXPERIMENTAL

In the process of synthesizing donor–acceptor compounds between TTF and metal complexes[10] we took the opportunity of obtaining single crystals of $(TTF)_3(BF_4)_2$ by the Wudl's procedure[5] followed by recrystallization in cold acetonitrile. Crystal data are as follows: black crystals, $C_{18}H_{12}B_2F_8S_{12}$, molecular weight 786.7; triclinic; $a = 8.017(3)$, $b = 8.601(1)$, $c = 11.635(2)$ Å, $\alpha = 108.79(1)$, $\beta = 100.96(2)$, $\gamma = 99.09(2)°$; $Z = 1$; $d_m = 1.81(1)$ (flotation), $d_{calcd} = 1.80$ g cm^{-3}; space group assumed to be $P\bar{1}$ on the basis of convincing intensity statistics.

Intensity data were collected in the $\omega/2\theta$ scan mode on a CAD4 Enraf Nonius automatic diffractometer using MoKα radiation ($\lambda = 0.71069$ Å). In the Bragg angle range $0 < \theta < 27°$, 3312 $\pm h \pm kl$ reflections were scanned using the variable-speed technique; on the basis of a fast prescan, 692 of them with $I < 1.3\sigma(I)$ were considered too weak to be measured. The 2620 observed reflections were merged into 2509 unique reflections; since only 67 of them had $I < 3\sigma(I)$, the full data set was used for structure solution and refinement. The usual Lorentz-polarization correction was applied but no correction was made for absorption (block-shaped crystal $0.3 \times 0.3 \times 0.3$ mm^3, $\mu_{MoK\alpha} = 8.8$ cm^{-1}).

The structure was solved by the direct methods[11] and refined by the full-matrix least-squares technique.[12] The non-hydrogen atoms were given anisotropic temperature factors and the hydrogen atoms were included at calculated positions ($d_{C-H} = 0.97$ Å) with a common isotropic temperature factor which converged to the value $U = 0.083(4)$ Å^2. The fluorine atoms of the BF_4^- anion are disordered and their parameters were approximated *via* a constrained refinement technique. The electronic distribution around the boron atom was interpreted as resulting from large oscillations of the fluorine atoms about three sets of equilibrium positions (F, F′, F″) with relative occupancy factors x, $(1 - x)/2$ and $(1 - x)/2$ respectively where x was refined to the final value of 0.39(2). The common B–F distance converged to 1.360(2) Å. The final conventional reliability indices were $R = \Sigma|k|F_0| - |F_c||/\Sigma k|F_0| = 0.028$ and $R_w = [\Sigma w(k|F_0| - |F_c|)^2/\Sigma wk^2|F_0|^2]^{1/2} = 0.037$ with $w = 2.1/(\sigma^2(F_0) + 0.0002F_0^2)$ for 257 variables. The highest peaks (< 0.5 e$^-$/Å^3) in the final difference Fourier map are all concentrated in the BF_4 region indicating that the model used in the refinement does not fully accommodate the random distribution of the fluorine atoms. Subsequently this will not be discussed further.

Positional parameters of the non-hydrogen atoms are listed in Table I. Tables of non-hydrogen atom anisotropic thermal parameters and hydrogen atom calculated positional parameters have been deposited

TABLE I

Final non-hydrogen atom positional parameters for $(TTF)_3(BF_4)_2$. Estimated standard deviations are indicated in parentheses

Atom	x/a	y/b	z/c
S(1)	.26257(6)	.94111(6)	.61799(5)
S(2)	.48462(6)	.71227(6)	.54220(5)
S(3)	.16676(6)	.94319(7)	.33214(5)
S(4)	.39486(7)	.71819(6)	.26533(5)
S(5)	.14756(6)	.38700(6)	.61700(5)
S(6)	−.07595(6)	.62898(6)	.67135(5)
C(1)	.3454(2)	.8290(2)	.5001(2)
C(2)	.3057(2)	.8302(2)	.3786(2)
C(3)	.3648(3)	.8693(3)	.7291(2)
C(4)	.4656(3)	.7637(3)	.6935(2)
C(5)	.1877(3)	.8835(3)	.1806(2)
C(6)	.2925(3)	.7798(3)	.1501(2)
C(7)	.0145(2)	.5033(2)	.5598(2)
C(8)	.1315(3)	.4716(3)	.7705(2)
C(9)	.0306(3)	.5793(3)	.7948(2)
B	.2928(3)	.2278(4)	−.0081(2)
F(1)	.451(1)	.189(2)	.017(1)
F(2)	.233(2)	.173(2)	−.1350(4)
F(3)	.189(1)	.156(1)	.050(1)
F(4)	.256(2)	.3835(8)	.0187(9)
F′(1)	.411(2)	.137(3)	.016(1)
F′(2)	.201(3)	.127(2)	−.1266(8)
F′(3)	.190(3)	.221(3)	.071(2)
F′(4)	.400(3)	.384(2)	.036(2)
F″(1)	.4638(8)	.287(2)	.056(1)
F″(2)	.299(2)	.219(2)	−.1257(6)
F″(3)	.206(2)	.072(1)	−.021(1)
F″(4)	.227(3)	.361(2)	.046(2)

along with a list of the observed and calculated structure factor amplitudes.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The structure consists of alternating layers of BF_4^- anions and of TTF species (Figure 1). Each TTF layer is built of parallel stacks of almost planar TTF entities piled up along the [110] direction and tilted by about 17 ° with respect to this direction (Figure 2). The sole interstack contact shorter than the sum of the van der Waals radii (3.70 Å) is S(2)...S(2; $1-x, 1-y, 1-z$) = 3.523 Å. All other interstack S...S

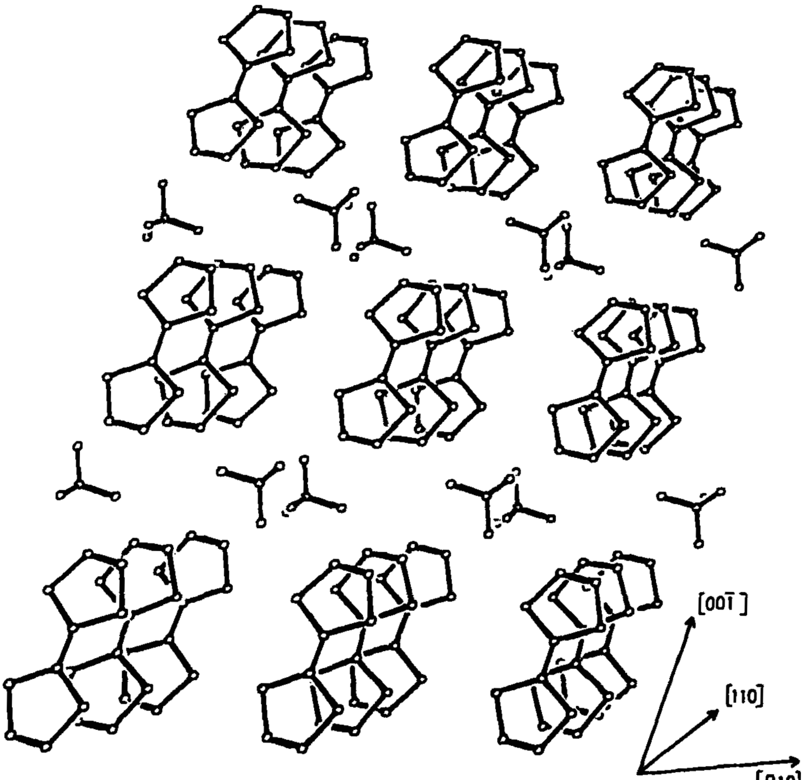


FIGURE 1 Perspective drawing[13] of the packing of the TTF and BF_4 entities. The BF_4^- anion is drawn in its 39% orientation. Hydrogen atoms are omitted in this and all subsequent figures.

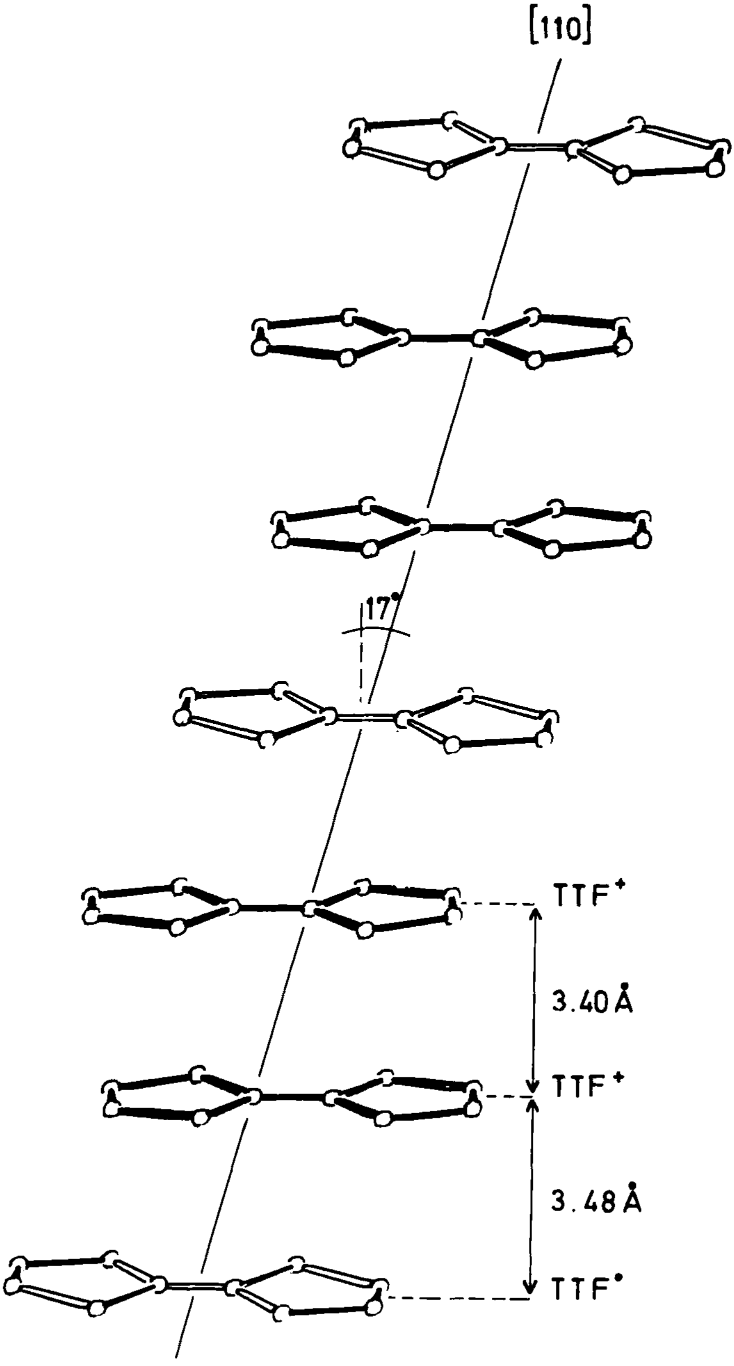


FIGURE 2 Side view of the stacking of the TTF species along the [110] direction (tilted by 15°).

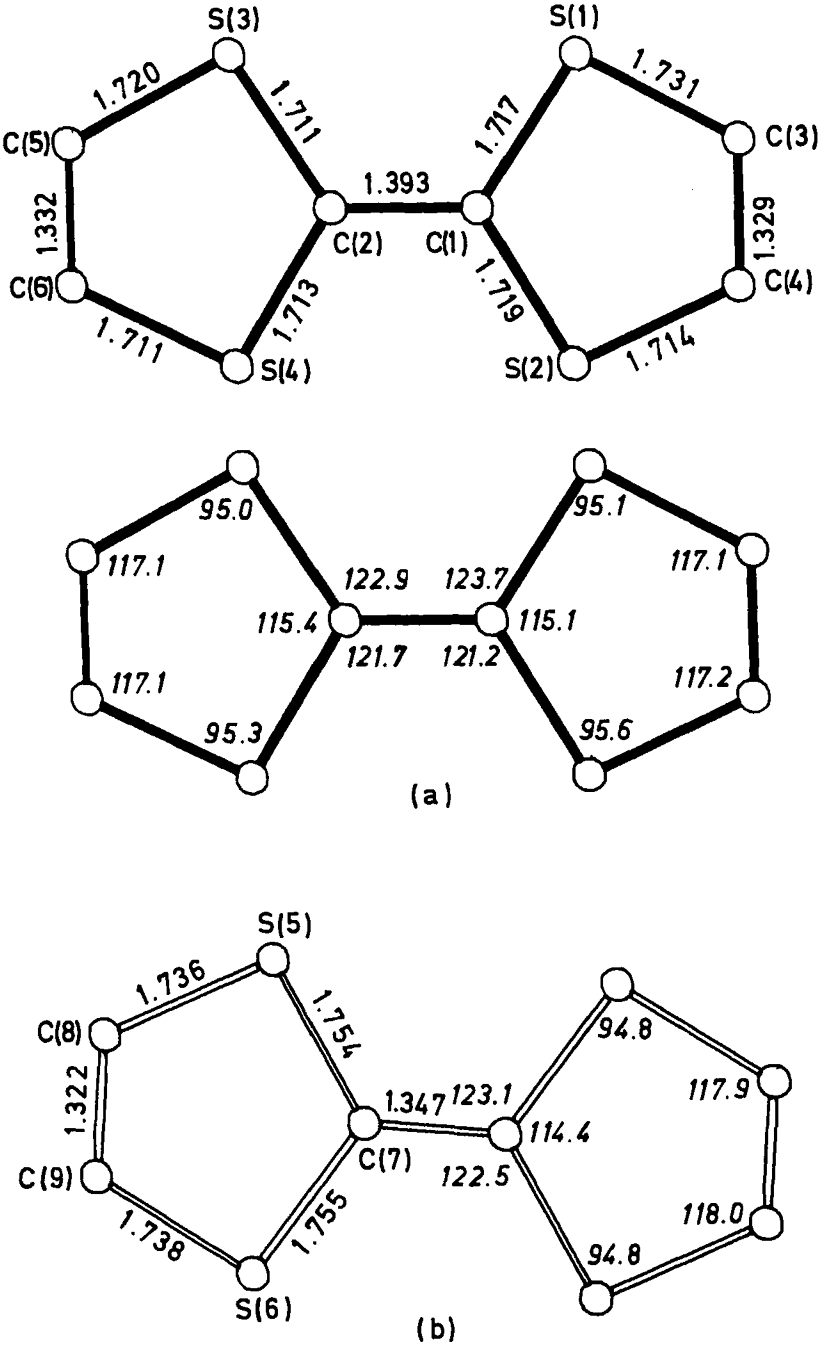


FIGURE 3 Bond lengths (Å) and bond angles (°) for TTF$^+$ (a) and TTF° (b). The standard deviations are 0.002 Å for C—S, 0.003 Å for C—C, 0.1° for C—S—C and S—C—S and 0.2° for C—C—S.

contacts fall in the range 3.825–3.874 Å. In contrast the average intermolecular intrastack distance is quite short (3.45 Å similar to that observed in (TTF)(TCNQ)[14]: 3.47 Å). The TTF species could be considered in a formally mixed valence state $TTF^{+0.67}$; however a closer look to the TTF stacking arrangement shows that each independent stack consists of $(TTF^+)_2$ diads interspersed with neutral TTF° monads. The TTF° molecules are readily distinguished from the TTF^+ cations by considering their respective geometry (Figure 3 and Table II).

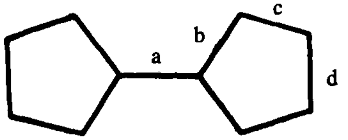
The TTF° molecule lies on a center of symmetry. Its geometry is quite similar to that observed in the TTF crystal.[15] The molecule is not strictly planar and exhibits the slight chair distortion usually encountered:[15,16] the central plane, defined by the sulphur and the central carbon atoms, makes an angle of 4.0° with the exterior plane defined by the sulphur and the end carbon atoms (Table III).

The TTF^+ ion is not centrosymmetric. The central C—C bond is much longer and the internal C—S bonds much shorter than in the TTF° molecule (and in the mixed valence TTF compounds quoted in Table II). The observed geometry is very close to that of TTF^+ in $(TTF)ClO_4$.[17]

The other features are related to the TTF stacking along [110] (Figure 2). The TTF° molecules alternate with $(TTF^+)_2$ diads made of two centrosymmetrically related TTF^+ cations with an interplanar distance of 3.40 Å. The TTF° and TTF^+ mean planes are almost parallel (dihedral angle 2.7°, Table III) but the interplanar distance is

TABLE II

Comparison of bond lengths (Å) in TTF averaged over assumed mmm symmetry



	TTF° in $(TTF)_3(BF_4)_2$	TTF	$(TTF)I_{0.71}$	(TTF) (DETCNQ)	(TTF) (TCNQ)	TTF^+ in $(TTF)_3(BF_4)_2$	(TTF) ClO_4
a	1.347	1.349	1.350	1.367	1.372	1.393	1.404
b	1.755	1.757	1.732	1.750	1.745	1.715	1.713
c	1.737	1.730	1.721	1.720	1.739	1.719	1.725
d	1.322	1.314	1.336	1.323	1.326	1.330	1.306
ref.	this work	15	6	16	14	this work	17

significantly longer: 3.48 Å indicating a weaker interaction. The TTF^+–TTF^+ overlap within a diad is of the ring-over-ring type (Figure 4a) while the TTF°–TTF^+ overlap is of the bond-over-ring type (Figure 4b); these result in a "stairs-like" stacking. As a consequence the two rings in an individual TTF^+ do not have the same environment and thus display slightly different geometries: the ring which interacts with only one ring of the other member of the diad is strictly planar while the ring which interacts with both a ring of the other TTF^+ and the central bond of the TTF° adopts a non-planar configuration (Table III).

The main features of the above description are to be compared with the literature data.

(i) *Geometry of the* $(TTF^+)_2$ *diads.* Fully eclipsed $(TTF^+)_2$ diads have already been observed, for example, in the low-conductive compounds (TTF)Br,[7] $(TTF)(TCNQF_2)$,[18] $(TTF)ClO_4$ [17] and $(TTF)_2NiS_4C_4H_4$.[19] The interplanar separations are 3.34, 3.34, 3.42 and 3.48 Å respectively; the geometry of the $(TTF^+)_2$ diad in $(TTF)_3(BF_4)_2$ is thus quite close to that in $(TTF)ClO_4$. The interplanar separations mentioned above are much shorter than those in the regular stacking of the highly conductive TTF halides: 3.56 Å for $(TTF)I_{0.71}$,[6] 3.57 Å for $(TTF)Br_{0.71-0.76}$,[7] 3.61–3.63 Å for $(TTF)SCN_{0.54-0.58}$.[8]

(ii) *Stacking.* To our knowledge a similar "stairs-like" stacking with alternation of ring-over-ring overlap within a $(TTF^+)_2$ diad and bond-over-ring overlap between TTF^+ and TTF° has never been observed to date. This holds true for analogs such as TMTTF, TMTSF[20].... Nevertheless, it should be noted that the stacking arrangements in $(TTF)_2NiS_4C_4H_4$ [19] and $(TTF)(TCNQF_2)$[18] show some similarities. In the first compound $(TTF^+)_2$ diads are separated by neutral TTF° molecules, all stacked along [010]. However, the $(TTF^+)_2$ diads and the TTF° molecules in the stacks are rotated by about 60° with respect to each other; moreover there is a third type of unstacked TTF° molecules. In $(TTF)(TCNQF_2)$ there is an alternation of ring-over-ring and bond-over-ring overlap involving however only TTF^+ cations.

In conclusion, the intramolecular intrastack distances in $(TTF)_3(BF_4)_2$ are not uniform at all (3.40 vs 3.48 Å) in contrast with the regular stacking observed in the conductive TTF halides.[6–8] In the highly conductive $(TMTSF)_2X$ series[2b,3,21] the observed slight alternation in "interdimer" distance ($\simeq$ 0.02 Å) is meaningless as noted by Wudl.[22] However it is true that in the $(TMTTF)_2X$ series[23–26] significant dimerization occurs for $X = SCN^-$ [24] and NO_3^- [26] ($\simeq$ 0.07 Å).

TABLE III

Deviations (Å) of atoms to their least-squares plane and dihedral angles (°). Primed atoms are in the $-x, 1-y, 1-z$ equivalent position

		(I) TTF° ring						(II) TTF° molecular plane			
S(5)	S(6)	C(7)	C(8)	C(9)		S(5)	S(6)	C(7)	C(8)	C(9)	
−.024	−.019	.023	.012	.007		−.046	−.037	−.019	.027	.024	
						S′(5)	S′(6)	C′(7)	C′(8)	C′(9)	
						.046	.037	.019	−.027	−.024	
		(III) TTF° central plane						(IV) TTF° exterior plane			
S(5)	S(6)	C(7)	C′(7)	S′(5)	S′(6)		S(5)	S(6)	C(8)	C(9)	
.000	.000	−.002	.002	−.000	−.000		−.001	.001	.003	−.003	
					TTF$^+$ rings						
		(V)						(VI)			
S(1)	S(2)	C(1)	C(3)	C(4)		S(3)	S(4)	C(2)	C(5)	C(6)	
.001	.013	−.014	−.001	−.007		−.001	−.000	.001	.001	−.001	
		(VII) TTF$^+$ molecular plane						(VIII) TTF$^+$ central plane			
S(1)	S(2)	S(3)	S(4)	C(1)		S(1)	S(2)	S(3)	S(4)	C(1)	C(2)
.030	.013	−.014	.007	.012		.010	−.008	−.008	.010	−.002	−.003
C(2)	C(3)	C(4)	C(5)	C(6)							
−.000	−.012	−.027	−.009	−.001							
					TTF$^+$ exterior planes						
		(IX)						(X)			
S(1)	S(2)	C(3)	C(4)			S(3)	S(4)	C(5)	C(6)		
−.001	.001	.003	−.003			−.000	.000	.001	−.001		

Dihedral angles

III–IV : 4.0; II–VII : 2.7; V–VI : 1.5; VIII–IX : 2.1; VIII–X : 0.5

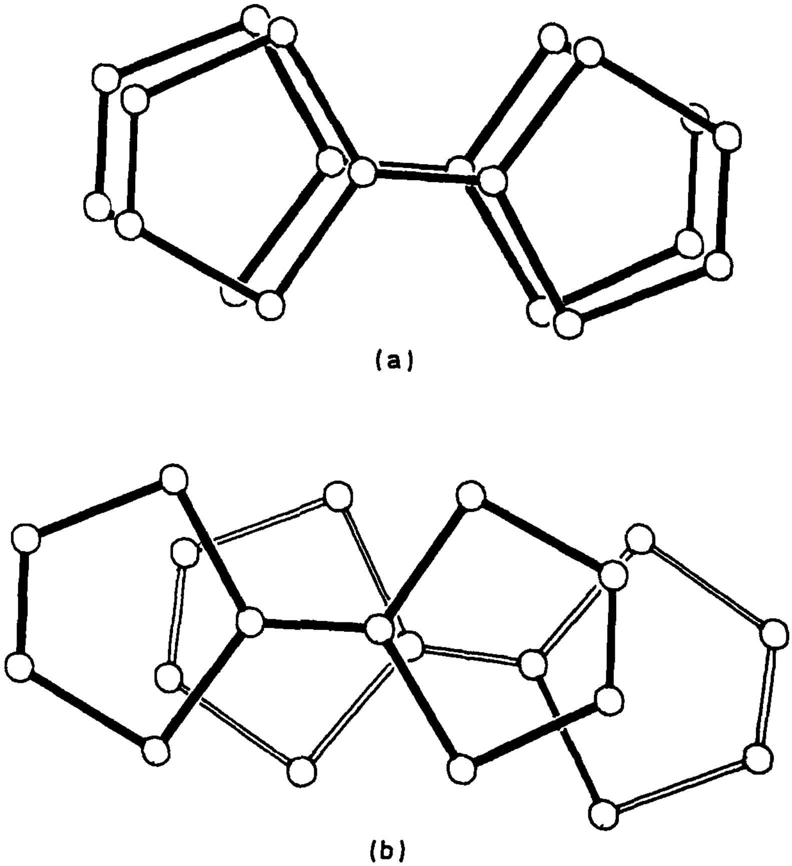


FIGURE 4 (a) TTF^+–TTF^+ overlap within a diad. (b) TTF°–TTF^+ overlap.

Therefore uniform stacking doesn't seem to be an absolutely discriminating condition for obtaining conductive species. More important is that in the TTF halides, as well as in the $(TMTSF)_2X$ and $(TMTTF)_2X$ series, the donor species are all undistinguishable: this reflects the delocalized mixed valence state character of these compounds. In $(TTF)_3(BF_4)_2$ by contrast, there exist two definitely different TTF entities, TTF^+ cations and TTF° neutral molecules and therefore, despite its apparently nonstoichiometric formula (i.e. $(TTF)(BF_4)_{0.67}$), this compound is not a mixed valence compound but a pseudo-completely-ionic salt, $(TTF^+)_2(TTF^\circ)(BF_4)_2$, which shows no partial oxidation state, and this clearly explains why it doesn't belong to the class of the highly conductive TTF salts.

SUPPLEMENTARY MATERIAL

Tables of non-hydrogen atom anisotropic thermal parameters, hydrogen atom positional parameters and observed and calculated structure factor amplitudes have been deposited. This material may be obtained by contacting Gordon and Breach, One Park Avenue, New York, NY 10016.

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